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(19) (CA) APPLICATION FOR CANADIAN PATENT (12)

(54) Preparation of Polypropylene Under High Pressure

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Notice: This application is as filed and may therefore contain an incomplete specification.



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INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES PATENTWESENS (PCT)

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(21) Internationales Aktenzeichen: PCT/EP92/02017  (22) Internationales Anmeldedatum: 2. September 1992 (02.09.92)		(74) Gemeinsamer Vertreter: BASF AKTIENGESELLSCHAFT; Carl-Bosch-Straße 38, D-6700 Ludwigshafen (DE).  (81) Bestimmungsstaaten: CA, FI, HU, JP, KR, NO, RU, US, europäisches Patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, SE).	
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(54) Title: HIGH-PRESSURE PROCESS FOR PRODUCING POLYPROPYLENE			
(54) Bezeichnung: VERFAHREN ZUR HERSTELLUNG VON POLYPROPYLEN UNTER HOCHDRUCK			
(57) Abstract			
A process is disclosed for producing homopolymers of propylene or copolymers of propylene with other olefins or their mixtures. Polymerisation is carried out under pressures from 100 to 3000 bars and at temperatures from 100 to 330° C, using as catalyst a metallocene catalyst system.			
(57) Zusammenfassung			
Verfahren zur Herstellung von Homopolymerisaten des Propylens oder Copolymerisaten des Propylens mit anderen Olefinen oder deren Mischungen, wobei man bei Drücken von 100 bis 3000 bar und bei Temperaturen von 100 bis 330° C polymerisiert und als Katalysator ein Metallocenkatalysatorsystem verwendet.			
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Preparation of polypropylene under high pressure

The present invention relates to a process for the preparation of homopolymers of propylene or copolymers of propylene with other olefins or mixtures thereof.

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Processes for the preparation of homo- and/or copolymers of propylene at low pressures and with the use of Ziegler catalyst systems are disclosed in, for example, EP-A 351 392 and EP-A 321 852. However, heterogeneous systems are present, the productivities are

10

unsatisfactory and the choice of comonomers is limited.

It is an object of the present invention to provide a process for the preparation of homo- and/or copolymers of propylene which does not have the stated disadvantages.

15

We have found that this object is achieved by a process for the preparation of homopolymers of propylene or copolymers of propylene with other olefins or mixtures thereof, wherein polymerization is carried out at from 100 to 3000 bar and at from 100 to 330°C and the catalyst used is a metallocene catalyst system.

20

These processes give linear homopolymers with propylene or linear copolymers which have short chain branches.

25

Cyclic olefins of 3 to 12, preferably 4 to 8, carbon atoms, dienes, in particular  $\alpha,\omega$ -dienes of 4 to 10 carbon atoms, such as hexa-1,5-diene, and olefins of 2 to 10 carbon atoms, preferably ethylene, butenes and hexenes, have proven suitable as olefins which can be copolymerized with propylene, the  $\alpha$ -olefins being particularly preferred. These olefins may also have aryl or hetero element substituents, such as styrene or unsaturated substituted silanes.

30

As a rule, these comonomers are used in amounts of from 0.1 to 99.9, preferably from 1 to 99, % by weight, based on the amount of propylene.

35

The catalysts used are metallocene catalyst systems which contain, among the active components, a

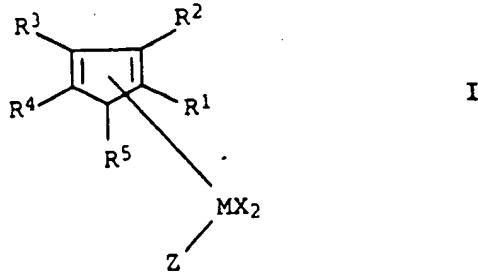
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complex of metals of subgroups IV and V of the Periodic Table, in particular of titanium, zirconium, hafnium, vanadium, niobium or tantalum. Preferably used complexes are those in which the metal atom is bonded via  $\pi$  bonds to unsaturated cyclic hydrocarbon atoms, for example cyclopentadienyl, fluorenyl or indenyl groups. Furthermore, in the preferably used complexes, the metal atom may also be bonded to further ligands, in particular to fluorine, chlorine, bromine and iodine or to C<sub>1</sub>-C<sub>10</sub>-alkyl, for example methyl, ethyl, propyl or butyl. Particularly suitable complexes contain in particular chlorine.

Preferred metallocene catalyst systems contain, as active components,

a) a metallocene complex of the general formula I

15



where

M is titanium, zirconium, hafnium, vanadium, niobium or tantalum,

20 X is fluorine, chlorine, bromine, iodine, hydrogen, C<sub>1</sub>-C<sub>10</sub>-alkyl, C<sub>6</sub>-C<sub>15</sub>-aryl or -OR<sup>6</sup>,

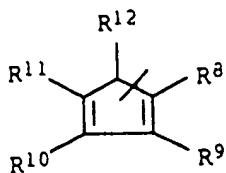
R<sup>6</sup> is C<sub>1</sub>-C<sub>10</sub>-alkyl, C<sub>6</sub>-C<sub>15</sub>-aryl, alkylaryl, arylalkyl, fluoroalkyl or fluoroaryl, each having from 1 to 10 carbon atoms in the alkyl radical and 6 to 20 carbon atoms in the aryl radical,

25 R<sup>1</sup> to R<sup>5</sup> are each hydrogen, C<sub>1</sub>-C<sub>10</sub>-alkyl, 5-membered to 7-membered cycloalkyl which in turn may carry a C<sub>1</sub>-C<sub>6</sub>-alkyl radical as a substituent, C<sub>6</sub>-C<sub>15</sub>-aryl or arylalkyl, where two adjacent radicals together may furthermore form unsaturated cyclic groups of 4 to 15 carbon atoms, or Si(R<sup>7</sup>),, R<sup>7</sup> is C<sub>1</sub>-C<sub>10</sub>-alkyl, C<sub>6</sub>-C<sub>15</sub>-aryl or C<sub>3</sub>-C<sub>10</sub>-cycloalkyl,

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Z is X or



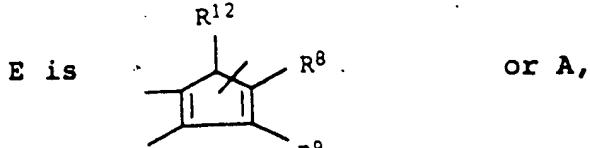
R<sup>8</sup> to R<sup>12</sup> are each hydrogen, C<sub>1</sub>-C<sub>10</sub>-alkyl, 5-membered to 7-membered cycloalkyl which in turn may carry a C<sub>1</sub>-C<sub>10</sub>-alkyl radical as a substituent, C<sub>6</sub>-C<sub>15</sub>-aryl or arylalkyl, and two adjacent radicals together may form cyclic groups of 4 to 15 carbon atoms, or Si(R<sup>13</sup>)<sub>3</sub>,

5

R<sup>13</sup> is C<sub>1</sub>-C<sub>10</sub>-alkyl, C<sub>6</sub>-C<sub>15</sub>-aryl or C<sub>3</sub>-C<sub>10</sub>-cycloalkyl, or R<sup>4</sup> and Z together form a group -[Y(R<sup>14</sup>)<sub>2</sub>]<sub>n</sub>-E-,

Y is silicon, germanium, tin or carbon,

10 R<sup>14</sup> is C<sub>1</sub>-C<sub>10</sub>-alkyl, C<sub>3</sub>-C<sub>10</sub>-cycloalkyl or C<sub>6</sub>-C<sub>10</sub>-cycloalkyl, n is 1, 2, 3 or 4,



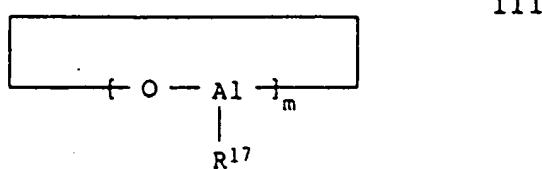
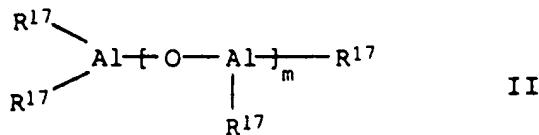
A is -O-, -S-, NR<sup>15</sup> or PR<sup>15</sup>,

15 R<sup>15</sup> is C<sub>1</sub>-C<sub>10</sub>-alkyl, C<sub>6</sub>-C<sub>15</sub>-aryl, C<sub>3</sub>-C<sub>10</sub>-cycloalkyl, alkylaryl or Si(R<sup>16</sup>)<sub>3</sub>, and

R<sup>16</sup> is C<sub>1</sub>-C<sub>10</sub>-alkyl, C<sub>6</sub>-C<sub>15</sub>-aryl, C<sub>3</sub>-C<sub>10</sub>-cycloalkyl or alkylaryl,

and

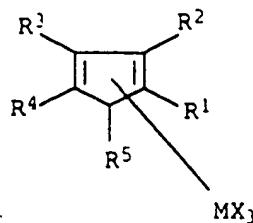
20 b) an open-chain or cyclic alumoxane compound of the general formula II or III



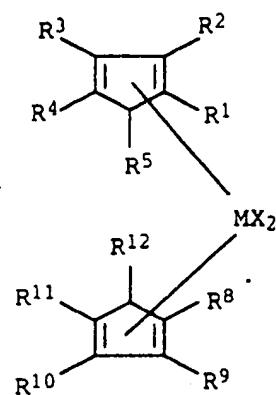
where  $R^{17}$  is  $C_1-C_4$ -alkyl and  $m$  is an integer of from 5 to 30.

Among the metallocene complexes of the general formula I,

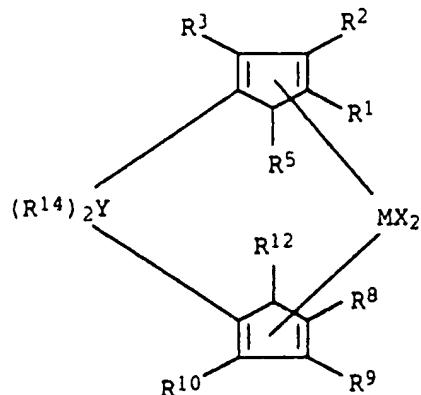
5



Ia

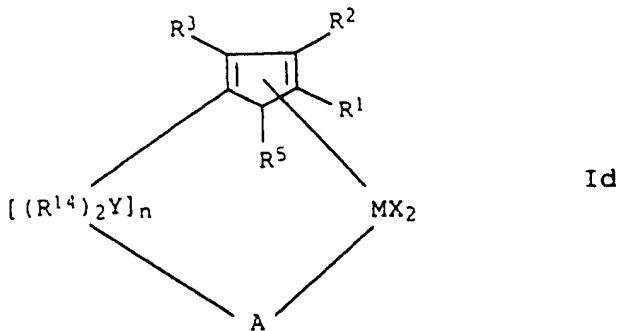


Ib



Ic and

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are preferred.

Paticularly preferred compounds of the formula Ia  
are those in which M is titanium, zirconium or hafnium,  
5 X is chlorine and R<sup>1</sup> to R<sup>5</sup> are each hydrogen or C<sub>1</sub>-C<sub>4</sub>-alkyl.

Particularly preferred compounds of the formula Ib  
10 are those in which M is zirconium or hafnium, X is  
chlorine, R<sup>1</sup> to R<sup>5</sup> are each hydrogen, C<sub>1</sub>-C<sub>4</sub>-alkyl or  
Si(R<sup>7</sup>), and R<sup>6</sup> to R<sup>10</sup> are each hydrogen, C<sub>1</sub>-C<sub>4</sub>-alkyl or  
Si(R<sup>13</sup>).

Particularly suitable compounds of the formula Ib  
15 are those in which the cyclopentadienyl radicals are  
identical, the unsubstituted cyclopentadienyl radicals  
being preferred.

Particularly suitable compounds of the formula Ic  
20 are those in which R<sup>1</sup> and R<sup>6</sup> are identical and are each  
hydrogen or C<sub>1</sub>-C<sub>10</sub>-alkyl, R<sup>5</sup> and R<sup>12</sup> are identical and are  
each hydrogen, methyl, ethyl, isopropyl or tert-butyl,  
R<sup>3</sup> and R<sup>10</sup> are C<sub>1</sub>-C<sub>4</sub>-alkyl, R<sup>2</sup> and R<sup>9</sup> are each hydrogen, or  
two adjacent radicals R<sup>2</sup> and R<sup>3</sup>, and R<sup>9</sup> and R<sup>10</sup>, together  
form unsaturated cyclic groups of 4 to 12 carbon atoms,  
R<sup>14</sup> is C<sub>1</sub>-C<sub>8</sub>-alkyl, M is zirconium or hafnium, Y is sili-  
con, germanium, tin or carbon and X is chlorine.

25 Examples of particularly suitable complexes  
include  
dimethylsilanediylbis-(3-tert-butyl-5-methylcyclopenta-  
dienyl)zirconium dichloride,

diethylsilanediylbis-(3-tert-butyl-5-methylcyclopenta-dienyl)zirconium dichloride,  
methylmethysilanediylbis-(3-tert-butyl-5-methylcyclo-pentadienyl)zirconium dichloride,  
5 dimethylsilanediylbis-(3-tert-butyl-5-ethylcyclopenta-dienyl)zirconium dichloride,  
dimethylsilanediylbis-(3-tert-butyl-5-methylcyclopenta-dienyl)dimethylzirconium,  
dimethylsilanediylbis-(2-methylindenyl)zirconium  
10 dichloride,  
diethylsilanediylbis-(2-methylindenyl)zirconium  
dichloride,  
dimethylsilanediylbis-(2-ethylindenyl)zirconium  
dichloride,  
15 dimethylsilanediylbis-(2-isopropylindenyl)zirconium  
dichloride,  
dimethylsilanediylbis-(2-tert-butyldindenyl)zirconium  
dichloride,  
diethylsilanediylbis-(2-methylindenyl)zirconium  
20 dibromide,  
dimethylsulfidebis-(2-methylindenyl)zirconium dichloride,  
dimethylsilanediylbis-(2-methyl-5-methylcyclopenta-dienyl)zirconium dichloride,  
dimethylsilanediylbis-(2-methyl-5-ethylcyclopenta-dienyl)zirconium dichloride,  
25 dimethylsilanediylbis-(2-ethyl-5-isopropylcyclopenta-dienyl)zirconium dichloride,  
dimethylsilanediylbis-(2-methylindenyl)zirconium  
dichloride,  
30 dimethylsilanediylbis-(2-methylbenzindenyl)zirconium  
dichloride and  
dimethylsilanediylbis-(2-methylindenyl)hafnium  
dichloride.

In the compounds of the general formula Id,  
35 particularly suitable ones are those in which M is  
zirconium or hafnium, X is chlorine or C<sub>1</sub>-C<sub>10</sub>-alkyl, Y is  
silicon or carbon when n is 1 or carbon when n is 2, R<sup>14</sup>

is  $C_1$ - $C_6$ -alkyl,  $C_1$ - or  $C_6$ -cycloalkyl or  $C_6$ - $C_{10}$ -aryl, A is  
-O-, -S- or  $\begin{array}{c} \diagdown \\ NR^{15} \end{array}$

and  $R^1$  to  $R^3$  and R' are each hydrogen,  $C_1$ - $C_{10}$ -alkyl,  $C_1$ - $C_{10}$ -cycloalkyl,  $C_6$ - $C_{15}$ -aryl or  $Si(R')$ .

5 Complexes of this type can be synthesized by conventional methods, the reaction of the correspondingly substituted, cyclic hydrocarbon anions with halides of titanium, zirconium, hafnium, vanadium, niobium or tantalum being preferred. Examples of corresponding preparation processes are described in, inter alia, Journal of Organometallic Chemistry 369 (1989), 359-370.

10 The metallocene complexes may also be present in cationic form, as described in EP-A 277 003 and EP-A 277 004.

15 In addition to the complexes, the metallocene catalyst systems generally also contain oligomeric alumoxane compounds of the general formula II or III, where  $R^{17}$  is preferably methyl or ethyl and m is from 10 to 25.

20 The preparation of these oligomeric alumoxane compounds is usually carried out by reacting a solution of trialkylaluminum with water and is described in, inter alia, EP-A 284 708 and US-A 4,794,096.

25 As a rule, the oligomeric alumoxane compounds obtained are in the form of mixtures of both linear and cyclic chain molecules of different lengths, so that m is to be regarded as an average value. The alumoxane compounds may also be present as a mixture with other metal alkyls, preferably with alkylaluminums.

30 In the novel process, it has proven advantageous to use the complex of metals of subgroups IV and V of the Periodic Table and the oligomeric alumoxane compounds in amounts such that the atomic ratio of aluminum from the oligomeric alumoxane compound to the transition metal from the complex of metals of subgroups IV and V of the Periodic Table is from 10 : 1 to  $10^6$  : 1, in particular

from 10 : 1 to  $10^4$  : 1.

For the novel process, the catalysts are generally used in an amount of from  $10^{-1}$  to  $10^{-9}$ , preferably from  $10^{-2}$  to  $10^{-5}$ , mol/l of metal.

5 The process can be carried out in the reactors usually used for high pressure polymerization, for example in stirred autoclaves.

10 It has proven advantageous first to mix the complex of metals of subgroups IV and V of the Periodic Table with the oligomeric alumoxane compound before the polymerization, with the result that an activated catalyst system is formed. The duration of the activation step is usually from 1 to 120 minutes, preferably from 10 to 100 minutes. Mixing is preferably carried out in such 15 a way that the complex is brought into contact with the solution of the oligomeric alumoxane compound in an inert solvent, for example in benzene, toluene, hexane, heptane or a mixture thereof, at from 0 to 50°C.

20 The novel process can be carried out by a method in which the solutions of complexes and oligomeric alumoxane compounds are mixed upstream of the reactor and/or are fed into the reactor at a plurality of points. The polymerization can be carried out batchwise or continuously. Pressures of from 100 to 3,500 bar, 25 preferably from 500 to 3,000, in particular from 1,000 to 3,000, bar and temperatures of from 100 to 330°C, preferably from 120 to 300°C, in particular from 120 to 250°C, are employed. The residence times are from 20 to 240, preferably from 30 to 120, seconds.

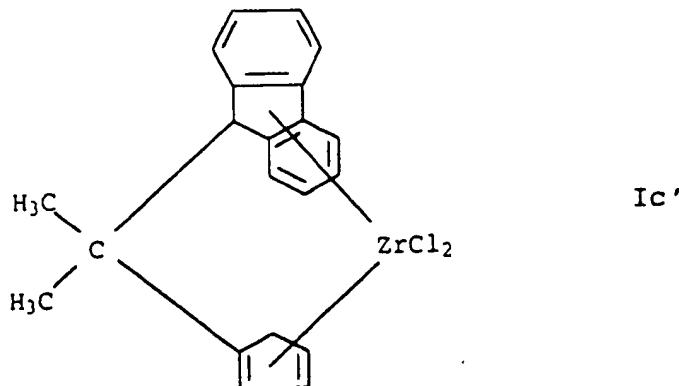
30 The essential advantages of the novel process are that high productivities are achieved, the choice of comonomers is very large and high conversions are reached in conjunction with short residence times and high molecular weights.

## EXAMPLES

## EXAMPLE 1

Preparation of a propylene homopolymer (PP)  
400 mg ( $\approx$  1 mmol) of

5



were dissolved in a mixture of 50 ml (36 g, 0.5 mol) of trimethylaluminum and 290 g of a 1.53 molar solution of methylalumoxane (0.5 mol) in 10 l of toluene. 10 m<sup>3</sup> of propylene/h and the solution described above were metered into a continuous high pressure stirred autoclave in the absence of air and moisture.

10

Table 1 shows the experimental conditions and the results.

15

The weight average molecular weight  $\bar{M}_w$  was determined by gel permeation chromatography.

TABLE 1

20

Temperature [°C]	Pressure [bar]	g Ic'/h	Residence time [min]	Productivity [g PP/g Ic'·h]	$\bar{M}_w$
149	1,510	0.17	1.5	8,380	2,000

25

## EXAMPLE 2

Preparation of a propylene/ethylene copolymer

The procedure described in Example 1 was followed, except that a mixture of propylene and ethylene was

polymerized.

Table 2 shows the experimental conditions and the results.

TABLE 2

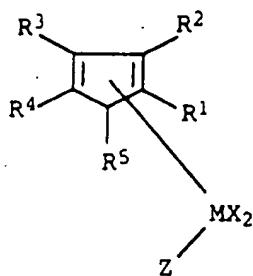
5  
10

Temperature [°C]	Pressure [bar]	g Ic'/h	% by wt. of propylene to % by wt. of ethylene in the gas mix- ture	Productivity [g polymer/ g Ic'·h]	$\overline{M}_w$
190	1,508	0.078	77/23	24,358	10,000

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We claim:-

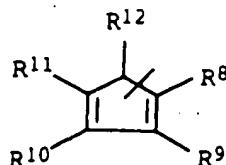
1. A process for the preparation of a homopolymer of propylene or of a copolymer of propylene with other olefins or mixtures thereof, wherein polymerization is carried out at from 100 to 3,000 bar and at from 100 to 330°C and the catalyst used is a metallocene catalyst system.
- 10 2. A process as claimed in claim 1, wherein a metallocene catalyst system is used which contains, as active components,
  - a) a metallocene complex of the formula I



I

where

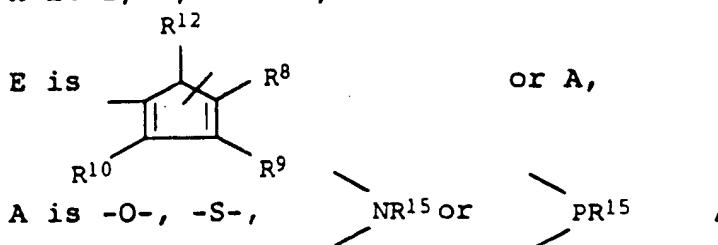
- M is titanium, zirconium, hafnium, vanadium, niobium or tantalum,
- 15 X is fluorine, chlorine, bromine, iodine, hydrogen, C<sub>1</sub>-C<sub>10</sub>-alkyl, C<sub>6</sub>-C<sub>15</sub>-aryl or -OR<sup>6</sup>,
- R<sup>6</sup> is C<sub>1</sub>-C<sub>10</sub>-alkyl, C<sub>6</sub>-C<sub>15</sub>-aryl, alkylaryl, arylalkyl, fluoroalkyl or fluoroaryl, each having from 1 to 10 carbon atoms in the alkyl radical and 6 to 20 carbon atoms in the aryl radical,
- 20 R<sup>1</sup> to R<sup>5</sup> are each hydrogen, C<sub>1</sub>-C<sub>10</sub>-alkyl, 5-membered to 7-membered cycloalkyl which in turn may carry a C<sub>1</sub>-C<sub>10</sub>-alkyl radical as a substituent, C<sub>6</sub>-C<sub>15</sub>-aryl or arylalkyl, where two adjacent radicals together may furthermore form cyclic groups of 4 to 15 carbon atoms, or Si(R<sup>7</sup>)<sub>2</sub>, R<sup>7</sup> is C<sub>1</sub>-C<sub>10</sub>-alkyl, C<sub>6</sub>-C<sub>15</sub>-aryl or C<sub>3</sub>-C<sub>10</sub>-cycloalkyl,
- 25 Z is X or



R<sup>8</sup> to R<sup>12</sup> are each hydrogen, C<sub>1</sub>-C<sub>10</sub>-alkyl, 5-membered to 7-membered cycloalkyl which in turn may carry a C<sub>1</sub>-C<sub>10</sub>-alkyl radical as a substituent, C<sub>6</sub>-C<sub>15</sub>-aryl or arylalkyl, and two adjacent radicals together may form cyclic groups of 4 to 15 carbon atoms, or Si(R<sup>13</sup>)<sub>3</sub>,

5 R<sup>13</sup> is C<sub>1</sub>-C<sub>10</sub>-alkyl, C<sub>6</sub>-C<sub>15</sub>-aryl or C<sub>3</sub>-C<sub>10</sub>-cycloalkyl, or R<sup>4</sup> and Z together form a group -[Y(R<sup>14</sup>)<sub>2</sub>]<sub>n</sub>-E-, Y is silicon, germanium, tin or carbon,

10 R<sup>14</sup> is C<sub>1</sub>-C<sub>10</sub>-alkyl, C<sub>3</sub>-C<sub>10</sub>-cycloalkyl or C<sub>6</sub>-C<sub>15</sub>-cycloalkyl, n is 1, 2, 3 or 4,



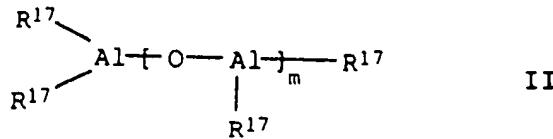
15 R<sup>15</sup> is C<sub>1</sub>-C<sub>10</sub>-alkyl, C<sub>6</sub>-C<sub>15</sub>-aryl, C<sub>3</sub>-C<sub>10</sub>-cycloalkyl, alkylaryl or Si(R<sup>16</sup>)<sub>3</sub>, and

R<sup>16</sup> is C<sub>1</sub>-C<sub>10</sub>-alkyl, C<sub>6</sub>-C<sub>15</sub>-aryl, C<sub>3</sub>-C<sub>10</sub>-cycloalkyl or alkylaryl,

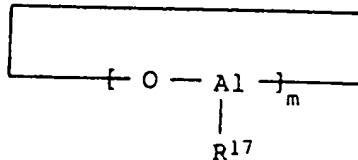
and

b) an open-chain or cyclic alumoxane compound of the formula II or III

20



III



where R<sup>17</sup> is C<sub>1</sub>-C<sub>4</sub>-alkyl and m is an integer of from 5 to 30.